PROCESS FLOW SHEET SIMULATION OF HYDROGEN PRODUCTION USING SULFUR-IODINE CYCLE

A PROJECT REPORT SUBMITTED IN THE PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF

Bachelor of Technology

in

CHEMICAL ENGINEERING

by

VENKATESH KATTAMURI

109CH0524

Department of Chemical Engineering

National Institute of Technology

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Under the guidance of

Prof. Madhusree Kundu

Department of Chemical Engineering
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CERTIFICATE

This is to certify that the thesis entitled **"PROCESS FLOW SHEET SIMULATION OF HYDROGEN PRODUCTION USING SULFUR-IODINE CYCLE"** submitted by Venkatesh Kattamuri in the partial fulfillment of the requirement for the award of BACHELOR OF TECHNOLOGY Degree in Chemical Engineering at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any degree or diploma.

Date:

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ACKNOWLEDGEMENT

I avail this opportunity to express my indebtedness to my guide **Prof. Madhusree Kundu**, Chemical Engineering Department, National Institute of Technology, Rourkela, for her valuable guidance, constant encouragement and kind help at various stages for the execution of this work. An erudite teacher, a strict disciplinarian, I consider myself fortunate to have worked under her supervision.

I also express my sincere gratitude to **Prof. R. K. Singh**, Head of The Department and **Prof. H. M. Jena**, Project Coordinator, Department of Chemical Engineering at NIT Rourkela for providing valuable department facilities.

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ABSTRACT

Today hydrogen (H_2) is considered as one of the most widely used new energy sources. The main reason for using H_2 as new energy sources over other sources are it is a non-pollution and reproducible gas-form energy carrier. International cooperation aims at delivering H_2 as a replacement fuel for vehicles. Hydrogen will be used as fuel for transport vehicles instead of gasoline/diesel oil/natural gas as fuel step by step in the future. The worldwide demand for hydrogen is about 50 million tons per year, and it is growing very rapidly. Many experts believe that hydrogen will overtake electricity as the preferred energy source.

The aim of the thesis was to develop the flow sheets for the entire Sulfur-Iodine thermochemical cycle for hydrogen production. There were three reactions in this cycle: Bunsen reaction, sulfuric acid decomposition and the hydriodic acid decomposition. The S-I cycle has been divided into three sections. They are (i) Section I, in which Bunsen reaction is the major and key step. (ii) Section II, H_2SO_4 concentration and decomposition are the major steps. (iii) Section III, here HI decomposition will takes place through the reactive distillation column. Optimization of each and every section was studied.

Keywords: Sulfur-Iodine Cycle, Bunsen Reaction, H_2SO_4 Decomposition, HI Decomposition.

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Chapter – 01

INTRODUCTION

1.1 HYDROGEN PRODUCTION USING THERMOCHEMICAL CYCLE:

It is well known that currently the main sources for the production of Hydrogen are natural gas and petroleum. There are many other processes by which hydrogen can be produced, but all these processes are not of primary interest, because all these processes are not economical and the main disadvantage associated with these is the emission of greenhouse which has a very strong adverse effect on human kind. The other major source for the production of Hydrogen is water. As the reaction is well known to all, this reaction will takes place by breaking the chemical bonds of water. . There are different methods through which hydrogen can be produced using water as a source. They are,

(i) Electrolysis

(ii) Direct thermal decomposition

(iii) Thermochemical cycles

Among these methods, the thermochemical cycle of water decomposition has receiving more attention due to the following advantages.

(i) In thermochemical cycles water is the only component which is used in the entire cycle and all other components will be recycled back to the system.

(ii) The emission of greenhouse gases is not at all possible in case of these cycles. This is the major disadvantage associated with other processes which makes the thermochemical cycles to receive more special attention among many research scientists.

(iii) Also it is found that the efficiency of these thermochemical cycles for production of H_2 is better than that of the other processes.

Thermochemical water decomposition cycle concept was proposed by Funk and Reinstrom (Funk and Reinstrom 1966). In a thermochemical process, thermal energy is transformed into chemical energy (hydrogen), without first converting heat to mechanical energy and then to electrical energy as is the case with electrolysis.

In the process of electrolysis, the steam process in which the heat form primary energy source gets converted into electrical energy is at best 40% efficient and the electrolysis process takes place with an efficiency of 90%. But the overall process took place at an efficiency of 36%.

Many types of thermochemical processes for hydrogen production have been proposed (Brown et al. 2003; Yalcin 1989). The selection of the SI cycle was based on a detailed literature search of published thermochemical cycles, a screening procedure using the criteria developed to rate each cycle, and a detailed analysis. The SI cycle is the cycle with the highest reported efficiency based on an integrated flow sheet. The Sulfur-Iodine (SI) or Iodine-Sulfur (IS) cycle is currently the major cycle which is being investigated in many countries. It has been studied extensively by the General Atomics (GA) (Brown et al. 2003; Norman et al. 1982) and the Japan Atomic Energy Research Institute (JAERI) (Kubo et al. 2004b; Kubo et al. 2004a; Nomura et al. 2005). In the present study, GA's SI cycle is chosen as a reference process.

1.2 SULFUR IODINE CYCLE:

The SI cycle consists of three chemical reactions which are given below.

Section I - $I_2+SO_2+2H_2O \rightarrow 2HI+H_2SO_4$

Section II - $H_2SO_4 \rightarrow H_2O+SO_2+1/2O_2$

Section III- $2HI \rightarrow H_2+I_2$

The net reaction of the S-I thermochemical cycle is the water splitting into hydrogen and oxygen.

$$H_2O \rightarrow H_2 + ½O_2$$

In S-I cycle except water all other process components will be recycled back and no greenhouse gases will be emitted which makes it more advantageous. The Sulfur Iodine cycle has been fully flow sheeted and operated at the bench scale in the US and Japan. It was found that the highest efficiency of 52% is noted in any process that has been fully flow sheeted. The production of hydrogen takes place at very high pressure, which eliminates the necessity of compressing the hydrogen for pipeline transmission or other processing.

One of the most challenging issues regarding the SI cycle are the material issues, which needs to withstand the very high process temperature 800-1000° Celsius. The main disadvantage associated with the S-I cycle is the reactants such as H_2SO_4 and HI are corrosive in nature. Also S-I cycle is very complicated in terms of plant size and some reactions in reactive distillation column will also form azeotrope.

1.3 SULFUR-IODINE CYCLE SIMULATION USING ASPEN PLUS:

In this report, the SI cycle simulation results using ASPEN PLUS code version 11 are presented. The present simulations followed the methodology applied to the GA's flow sheet (Brown et al. 2003). A step-by-step simulation is conducted to minimize the convergence problem in a complex system of the SI thermochemical process; the simulation is performed initially for the single

component. If adjacent components are converged, then they are combined and simulated. Finally, the simulation for the whole Section is conducted.

Chapter – 02

LITERATURE REVIEW

2.1 GENERAL ATOMICS (GA) S-I CYCLE:

General Atomics (GA) developed the SI cycle which offers the potential for efficient, cost-effective, large-scale production of hydrogen from water, in which the primary energy input is high temperature heat from an advanced nuclear reactor. GA developed the S-I process model based on the earlier flow sheets of individual Sections. They divided the S-I cycle into three sections. They are

(i) Section I – Bunsen reaction

(ii) Section II – H_2SO_4 concentration and decomposition

(iii) Section III- HI decomposition

Sulfuric acid and hydrogen iodide are generated in the low temperature exothermic Bunsen reaction (Section I).

Section I generates H_2SO_4 and HI at very low temperature and the reaction is exothermic. H_2SO_4 generated in Section I is sent to Section II and there it is concentrated by increasing the pressure in the separators and then the water free H_2SO_4 is decomposed. The reaction is endothermic in Section II. This reaction took place at very high temperatures. Coming to Section III, HI generated from Section I is decomposed in reactive distillation column and this reaction is endothermic and it requires medium temperature.

There are significant chemical separations associated with each chemical reaction. Water is the primary solvent in the system and iodine is also an important solvent in the Bunsen reaction.

GA’s earlier S-I cycle flow sheets were developed using hand calculation and the thermodynamic models present at that time could not deal with the non-ideality of the process. Recently they used Aspen Plus, which has the best implementation of the electrolytic solutions and their thermodynamics. It has

the capability of modeling electrolytes via several different modeling techniques including an electrolytic version of the Non-Random Two Liquid (NRTL) technique. An electrolytic NRTL (ELECNRTL) model can handle everything from concentrated electrolytes through dilute electrolytes to non-polar species, such as iodine.

Initially GA tried to develop new model for the entire section which has the ability to cover all the ranges of temperature. Since the thermodynamics of each and every part has a huge difference, they are not able to find such a kind of model which can simulate the entire section. With the help of Aspen Technology, they developed the NRTL model and it was used as a base thermodynamic model in Section II of the flow sheet.

However they are unable to develop new model for Section I and Section III. So the flow sheets for Section I and III were based on earlier analysis and they are done without using computer simulation program. For Section III, in which HI decomposition took place GA used Reactive Distillation process proposed by Roth and Knoche.

Very high temperature of 827°C is used in Section II and H_2SO_4 decomposition took place at this temperature in a compact heat exchanger which is a jacketed CSTR. The other two sections, Section I took at a temperature of around 100° C and Section III took place at a temperature of 500-600°C. They have estimated that 52% efficient production of H_2 will took place at a temperature of 900-950°C.

2.2 SECTION I:

S-I cycle was initially developed in mid-1970's, but it was rejected because of the difficulties that were encountered in separating the HI and H_2SO_4 produced

in the Bunsen Reaction. They also tried using distillation but it was found to be useless as H_2SO_4 and HI react according to the reverse of Bunsen Reaction when the mixture was heated. It was found that using excess of molten Iodine resulted in the separation of the two phase solution; one is a light phase containing H_2SO_4 and a heavy phase containing HI and I_2. GA's flow sheet for section I is shown in **Figure 1** The composition of streams Section I can be predicted from the thermodynamics but the properties of streams recycled back to Section I can only be determined after completing the detailed flow sheets of Section II and Section III.

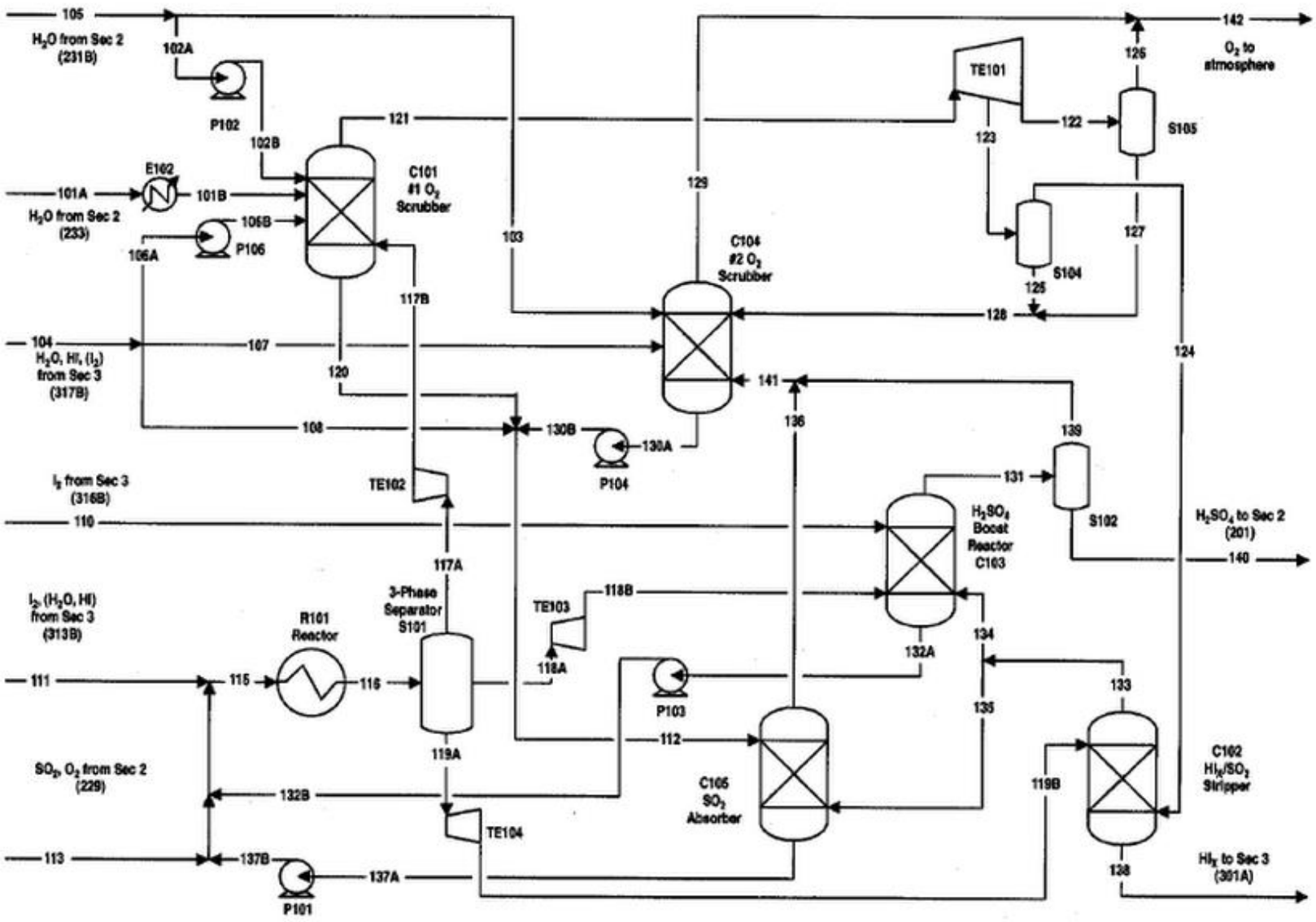


Figure 1: GA's Section I Flow Sheet

2.3 SECTION II:

The flow sheet for the Section II is shown in **Figure 2**. The purpose of Section II is to concentrate the H_2SO_4 received from the Section I and it gets decomposed producing SO_2 and O_2. It is important to concentrate before it is

sent for decomposition. Firstly, less material is heated to high temperatures means less sensible heat must be supplied, which means smaller heat exchangers and less cost. Secondly, there is a thermodynamics loss associated with the heat exchangers and lower heat transfer means it results in higher efficiency.

2.3.1 CONCENTRATION OF SULFURIC ACID:

The inlet H_2SO_4 of 20 mol% along with the internally recycled H_2SO_4 is concentrated up to 40% in a high pressure four stage isobaric concentrator. There the H_2SO_4 solution flows through four connected and heated chambers. In each chamber, water is boiled off so that the temperature and the acid concentration will increase as solution moves through each and every concentrator. The flow sheet developed by GA for the entire section II is shown in Fig . After concentration, the solution is used for decomposition.

2.3.2 DECOMPOSITION OF SULFURIC ACID:

Before the sulfuric acid can be decomposed, it must first be heated to the vaporization temperature and vaporized. All of these steps occur at 7 bars. The first step in the reaction sequence is the vaporization of the concentrated sulfuric acid stream. Some of the heat required to preheat the stream prior to vaporization is recovered from the liquid product of the isobaric concentrator but the remainder of the heat required for heating, vaporizing, and decomposing the sulfuric acid is provided by the high temperature helium from the nuclear reactor. From here the output products will be recycled back to the Section I.

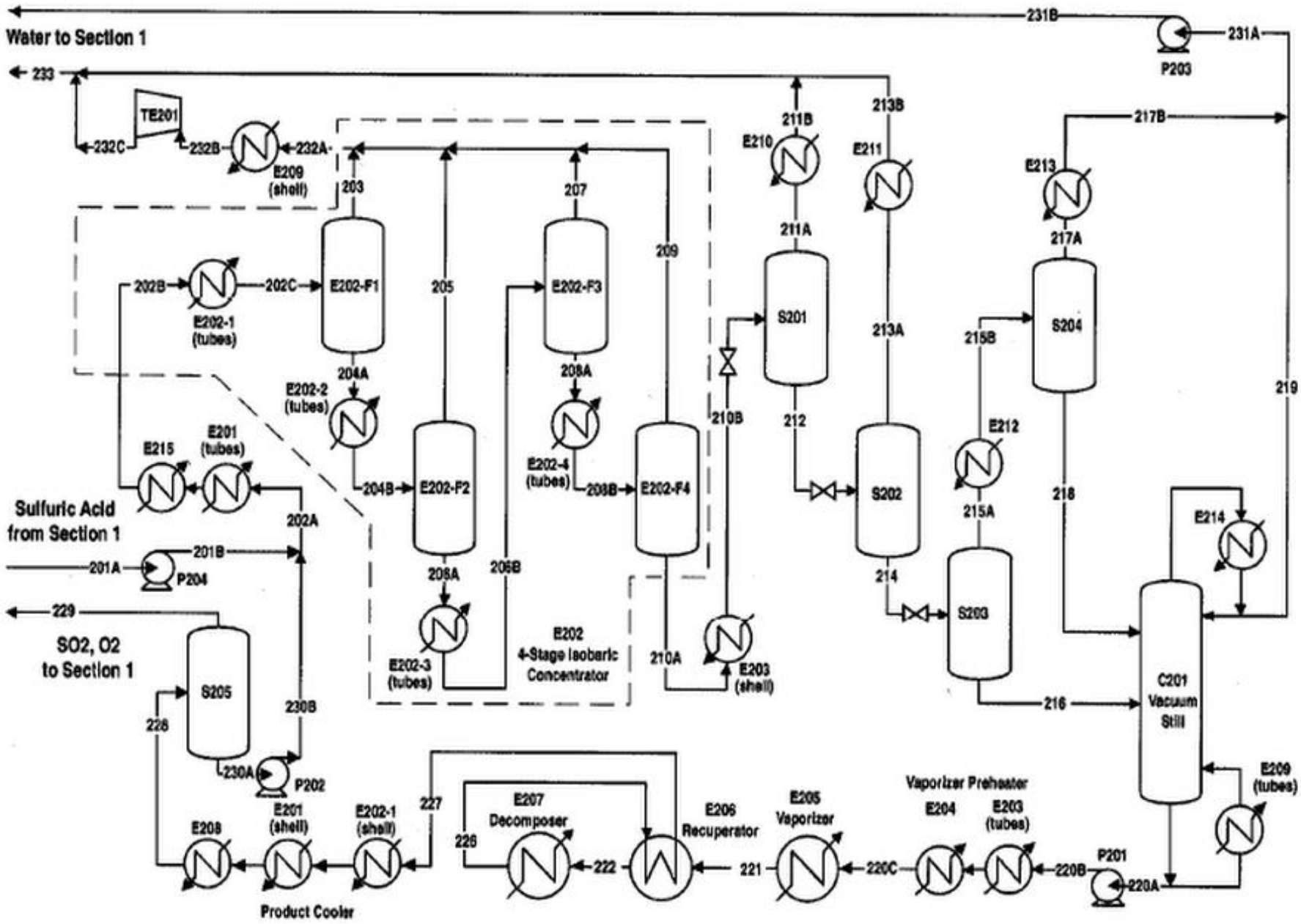


Figure 2: GA's Section II Flow sheet

2.4 SECTION III:

GA's earlier flow sheets developed in 1979 and 1981 (Norman et al. 1982) used phosphoric acid (H_3PO_4) to extract the water from the HI_x ($HI/I_2/H_2O$) solution resulting from the Bunsen reaction. It was indicated that over 40% of the total capital cost of the SI process was associated with the phosphoric acid concentration step. There have been a number of suggestions as to methods of modifying the process to reduce the capital cost.

In the initial stages of developing S-I cycle GA used H_3PO_4 to extract the water from HI_x solution which comes from the Bunsen reaction. It was found that more than 45% of the total capital cost of the S-I process was associated

with this H_3PO_4 concentration step and separation step. So many methods were suggested and modified to reduce the capital cost by reducing the cost associated with this step.

The methods proposed included the use of HBr at elevated pressure, to extract HI from the HI_x and using reactive distillation column to produce H_2 at elevated pressures. But later it is found that HBr usage also remains to be unsuccessful in the reduction of cost because of thermodynamics associated with this. Therefore later another method which uses reactive distillation came into focus and it was developed accordingly by GA.

2.4.1 GA'S HI DECOMPOSITION PROCESS:

GA's HI decomposition process is based on the reactive distillation flow sheet developed by Roth and Knoche. Since GA's HI concentration and decomposition scheme developed in 1981 seems to be the most expensive and energy consuming step, an alternative has been developed, in which HI is decomposed directly from liquid $H_2O/HI/I_2$ solution under high pressure and temperature. GA tried to regress the VLE and LLE data for the mixture of $HI/I_2/H_2O$, but they failed to obtain the useful results because of incomplete data. Also the decomposition of HI was under the measurement conditions, the total vapor measurements also included the equilibrium H_2 pressure. So HI decomposition process was simulated using the reactive distillation column. The flow sheet of the entire section III is given below in **Figure 4** and it is compare with the actual reactive distillation column which were used in early investigation and they both seems to be similar. **Figure 3** shows the actual reactive distillation column that was proposed by Roth and Knoche.

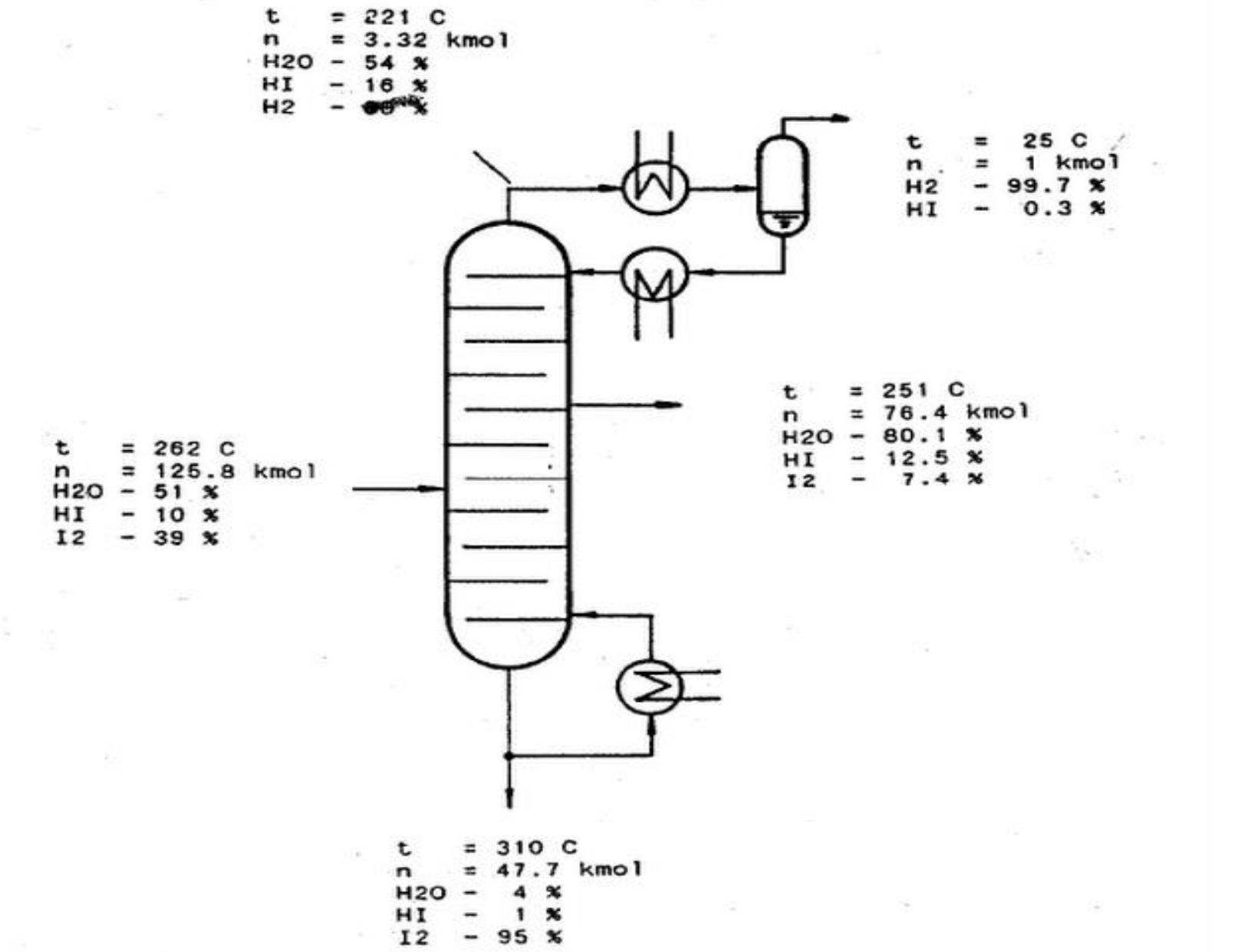


Figure 3: Reactive Distillation Column

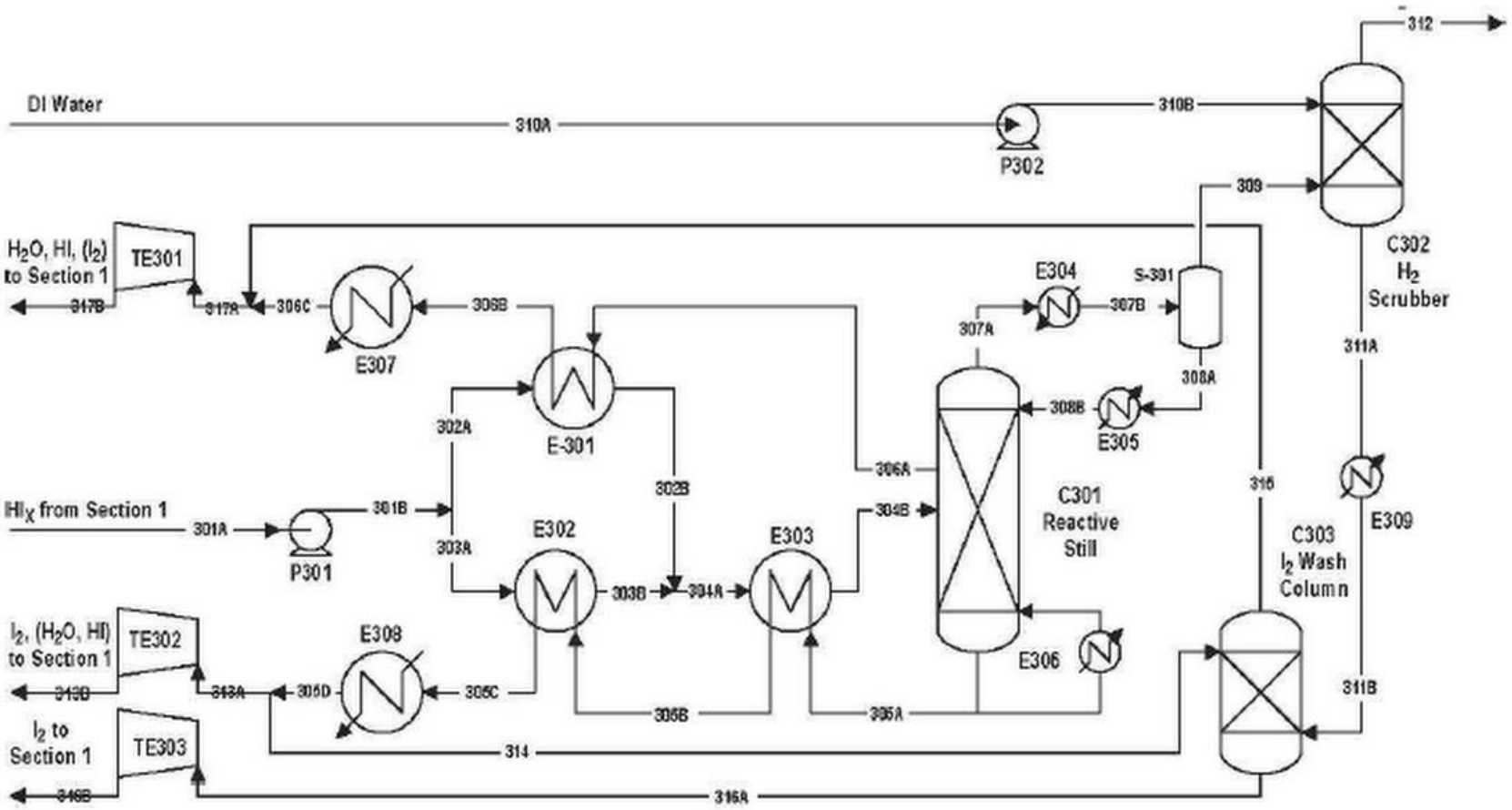


Figure 4: GA's Section III flow Sheet

For every mole of HI decomposed, five moles of HI are recycled unreacted and each mole of HI in the feed is accompanied by almost 4 moles of I_2 and

over 5 moles of water. Even so, this version of the process is more efficient than the version using H_3PO_4 as it is not necessary to vaporize the water.

Chapter – 03

Sulfuric Acid Decomposition of S-I cycle

3.1 SIMULATION USING ASPEN PLUS:

In this chapter, the ASPEN PLUS simulations results for the Section II of the S-I cycle are presented. The present simulations follow the methodology applied to the GA's Flow sheet. In order to minimize the convergence problem in such a complex system of S-I thermochemical processes. The simulation is performed initially for the single component, if adjacent components are converged, then they are combined and simulated. Finally, the simulation of whole section is conducted. The simulations were conducted and these are presented in detail. Firstly Section II is simulated using the data from literature. Then Section I followed by Section III were studied.

Section II is divided into two parts

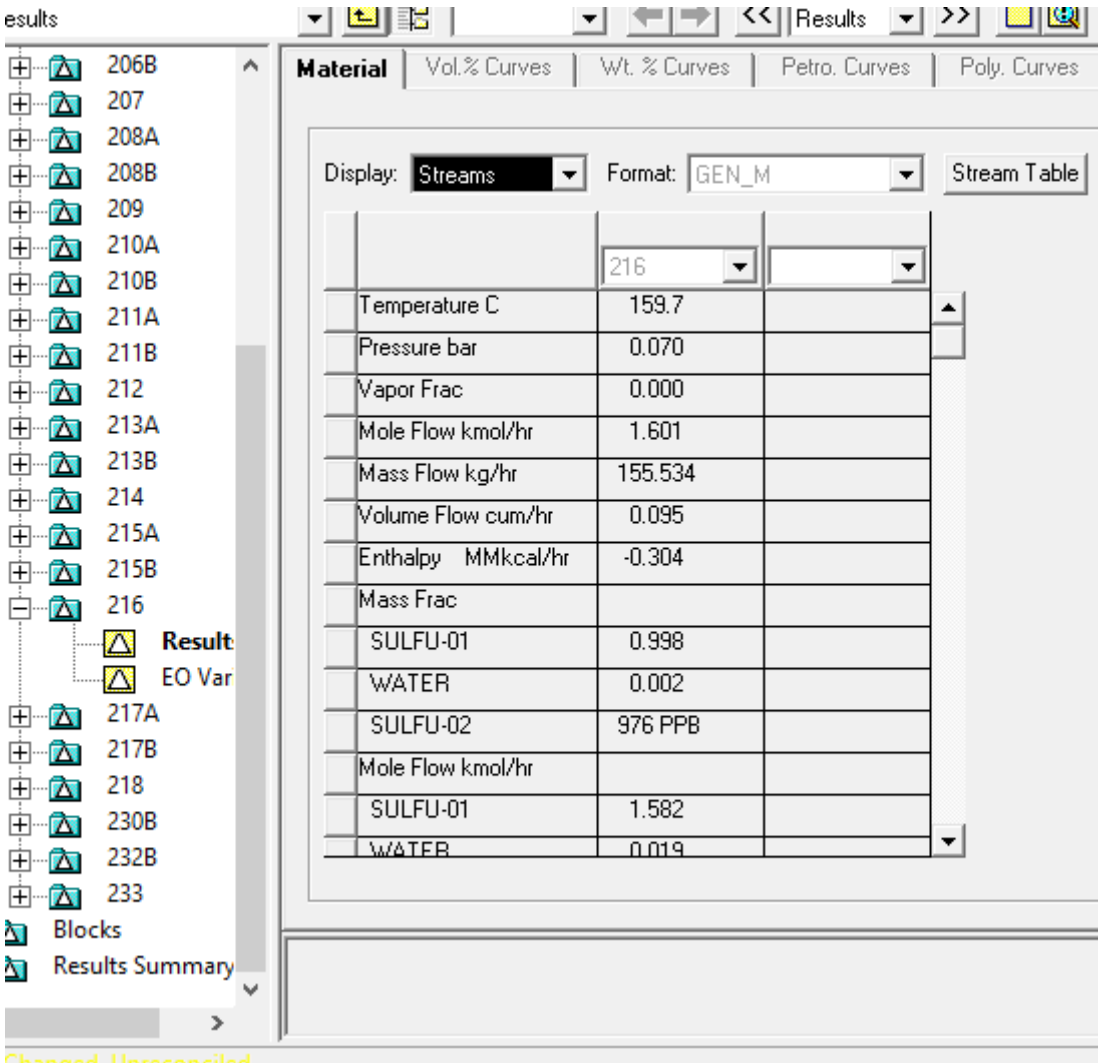
(i) H_2SO_4 concentration part

(ii) H_2SO_4 decomposition part

3.2 SECTION II CONCENTRATION PART:

The inlet stream coming fed to the Section II is from the Section II which is the stream 140. Then the pressure of the stream is raised by using a pump and it is then mixed with the recycle feed coming from the section II. The total input stream has a mass fraction of 0.576 H_2SO_4 concentration. The mass fraction of the H_2SO_4 in the stream 216 is 0.998 which clearly says that H_2SO_4 is concentrated and the results are in accordingly with the GA's results. The whole section of concentration is simulated and the flow sheet of concentration part is given in **Figure 5**. Table 1 gives the concentration profile of the output stream resulted after the concentration part. **Figure 6** shows the result showing that the entire flow sheet was converged without any errors. Table 2 shows the stream table resulted after the entire simulation.

Table1: Concentration Profiles of Sulfuric acid in input and output stream



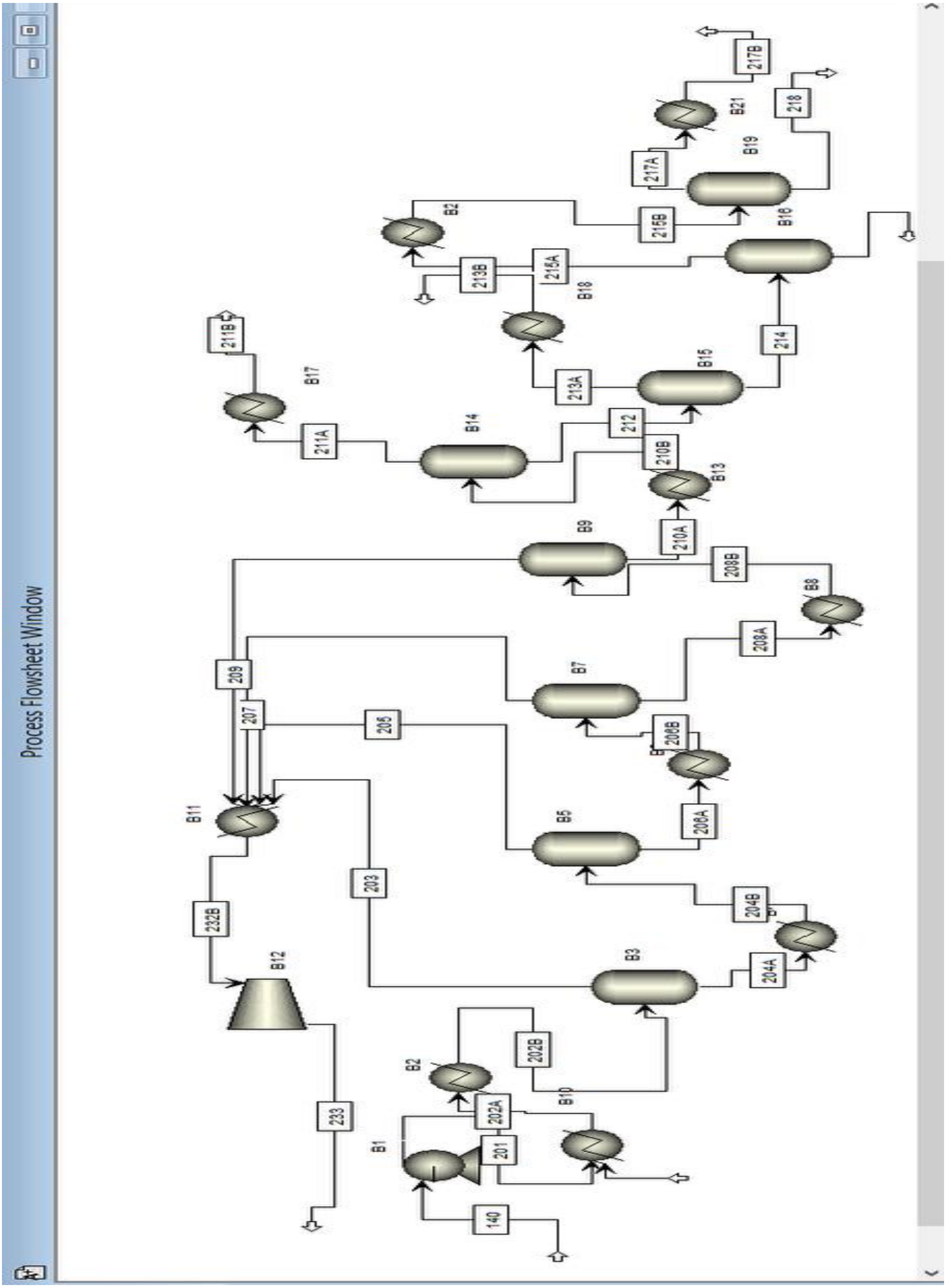


Figure 5: Flow sheet of H_2SO_4 concentration in Section II

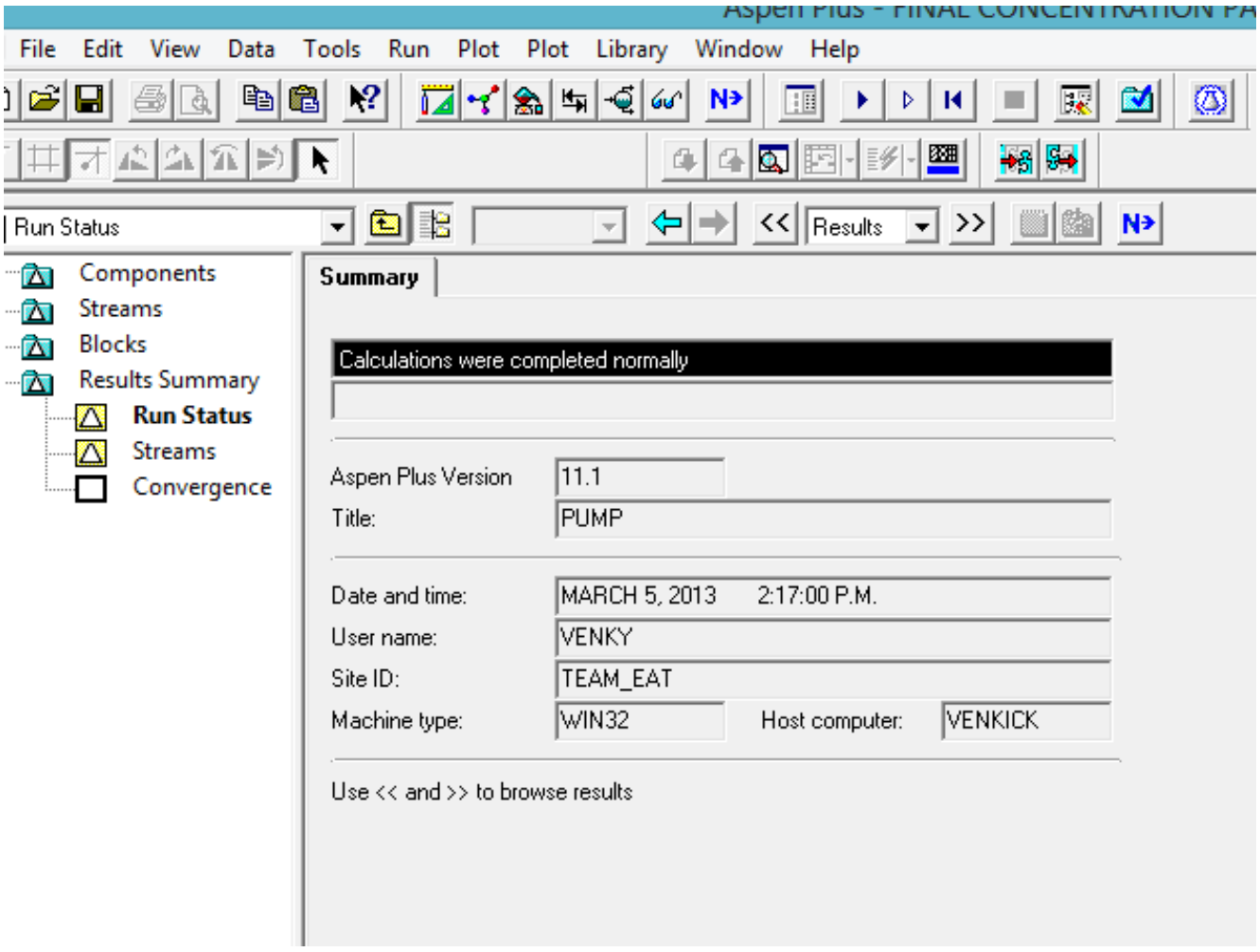


Figure 6: Result showing simulation is successful

Table 2: Stream Table after the Simulation

	A	B	C	F	G	H	I	J
1	Strear	H2O	H2SO4	SO2	Total	Phase	Presuure(Bar)	Temp K
2	140	4.094	1.023	0.004	5.121	L	1.85	384.5
3	201	4.094	1.023	0.004	5.121	L	35	393.15
4	202A	5.236	1.63	0.008	6.874	L	35	572.15
5	202B	5.236	1.63	0.008	6.874	L+V	603.15	603.15
6	203	4.385	0.036	0.007	4.428	V	35	603.15
7	204A	0.851	1.594	0.001	2.446	L	35	603.15
8	204B	0.851	1.594	0.001	2.446	L+V	35	619.15
9	205	0.161	0.002	0.001	0.164	V	35	619.15
10	206A	0.69	1.592	0.001	2.283	V	35	619.15
11	206B	0.69	1.592	<0.001	2.282	L+V	35	631.15
12	207	0.08	0.001	<0.001	0.081	V	35	631.15
13	208A	0.61	1.59	0.001	2.201	L	35	631.15
14	208B	0.61	1.59	0.001	2.201	L+V	35	644.15
15	209	0.016	<0.001	<0.001	0.016	V	35	644.15
16	210A	0.594	1.59	0.001	2.185	L	35	644.15
17	210B	0.594	1.59	0.001	2.185	L	35	581.15
18	211A	0.358	0.005	0.001	0.364	V	8	562.85
19	211B	0.358	0.005	0.001	0.364	L	8	393.15
20	212	0.237	1.585	<0.001	1.822	L	8	562.85
21	213A	0.132	0.002	<0.001	0.134	V	2	517.05
22	213B	0.132	0.002	<0.001	0.134	L	2	393.15
23	214	0.105	1.58	<0.001	1.685	L	2	517.05
24	215A	0.086	0.001	<0.001	0.087	V	0.07	432.85
25	215B	0.086	0.001	<0.001	0.087	V+L	0.07	408.15
26	216	0.019	1.582	TRACE	1.601	L	0.07	432.85
27	217A	0.086	<0.001	<0.001	0.086	V	0.07	408.15
28	217B	0.086	<0.001	<0.001	0.086	L	0.07	311.15
29	218	<0.001	0.001	TRACE	0.001	L	0.07	408.15
30	230B	1.142	0.606	0.004	1.752	L	35	396.015
31	232B	4.642	0.04	0.007	4.689	L	35	393.15
32	233	4.642	0.04	0.007	4.689	L	5.2	393.15

3.3 SECTION II DECOMPOSITION PART:

In Section II decomposition part, the input coming from the previous part, it means that the concentrated acid resulted after concentration comes to the RGibbs reactor and there the decomposition reaction took place. A total of 6 RGibbs reactor were used and among them the first three are used for the first reaction and the following reactors were used for the second reaction.

$$H_2SO_4 \rightarrow H_2O + SO_3$$

$$SO_3 \rightarrow SO_2 + 1/2\ O_2$$

The reactors were operated at very high temperature of around 800-900°C. In the entire S-I cycle the part where highest temperature recorded is this part and hence this part consumes a lot of energy and such a large or huge amount of energy comes from the advanced helium nuclear reactor. The section II Decomposition part also simulated as per the same convergence rule. At first single parts are converged and then they are joined together likely the whole plant simulation is completed. **Figure 7** shows the flow sheet for Section II where decomposition is the major step. Table 3 shows the stream table of decomposition part of the Section II. Table 4 shows the input and output streams of the output stream. It is clear that the concentration of sulfuric acid is very less showing clearly how decomposition took place.

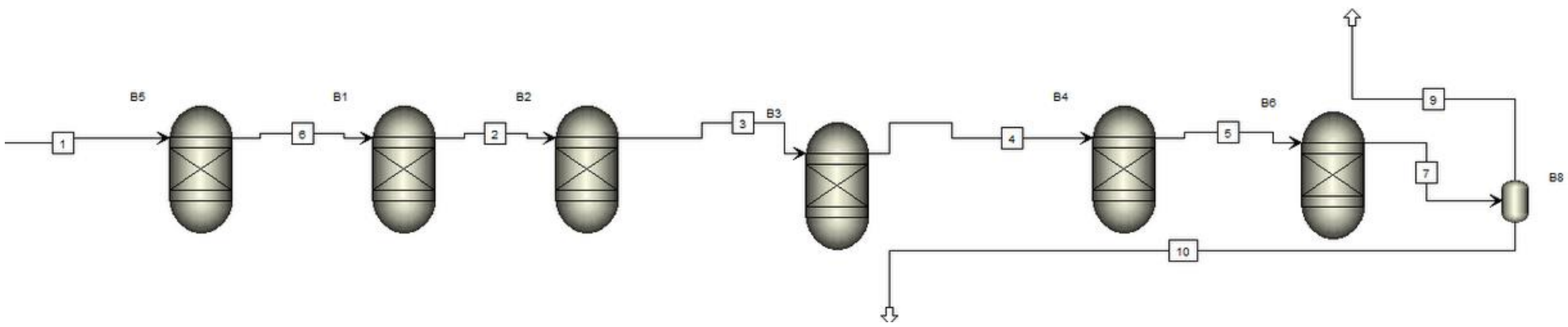


Figure 7: Flow sheet of Section II decomposition Part

Table 3: stream table of Section II decomposition part

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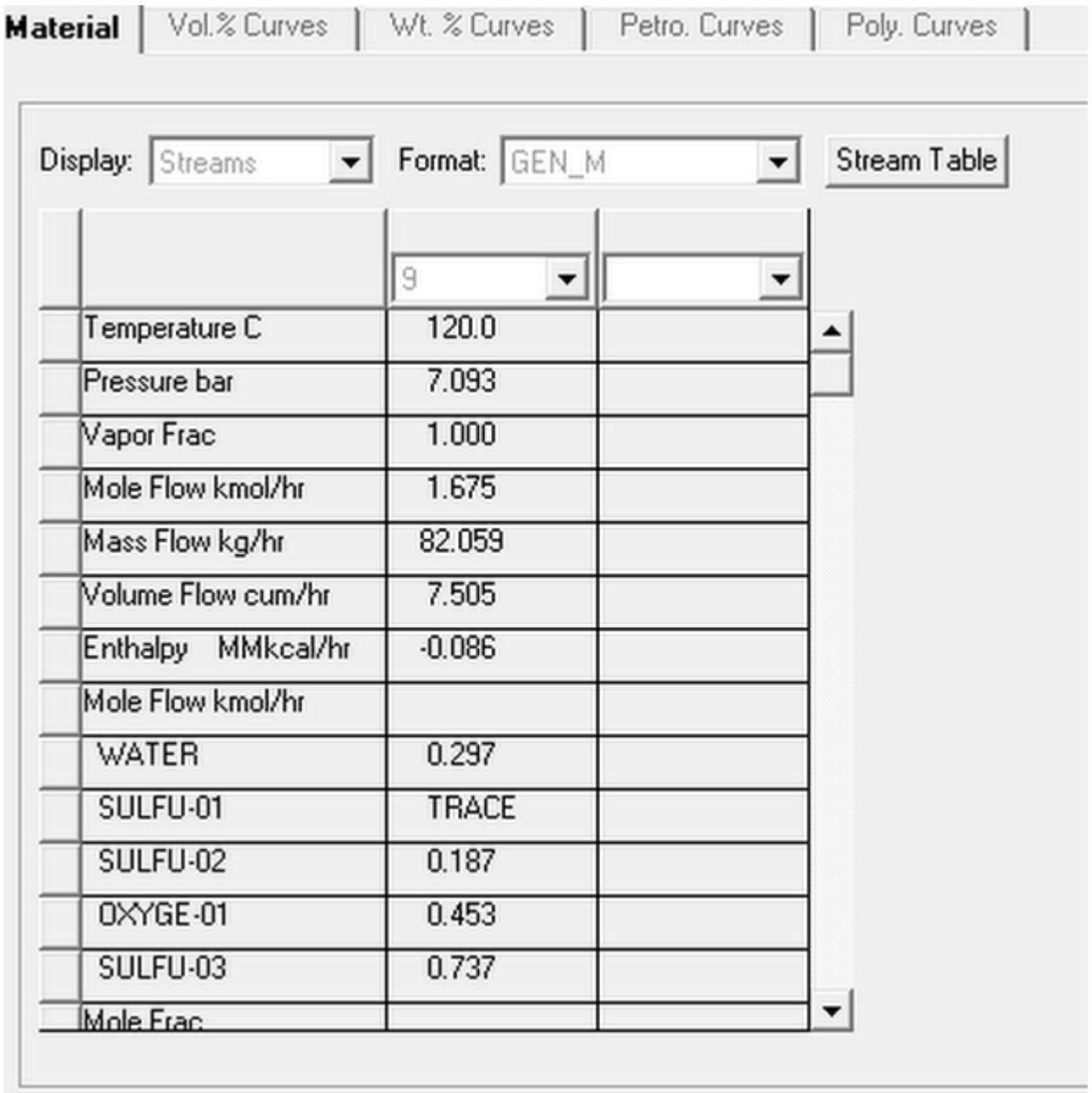
Stream ID		1	2	3	4	5	6	7	9	10
Temperature	C	411.0	601.9	681.9	751.9	827.0	796.9	431.0	120.0	120.0
Pressure	bar	7.000	7.000	7.000	7.000	7.000	7.000	7.000	7.093	7.093
Vapor Frac		0.607	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.000
Mole Flow	kmol/hr	2.224	3.424	3.611	3.755	3.890	3.839	3.448	1.675	1.773
Mass Flow	kg/hr	160.700	160.700	160.700	160.700	160.700	160.700	160.690	82.059	78.631
Volume Flow	cum/hr	10.798	35.432	40.851	45.638	50.788	48.735	28.545	7.505	0.061
Enthalpy	MMkcal/hr	-0.278	-0.227	-0.217	-0.207	-0.197	-0.201	-0.226	-0.086	-0.173
Mole Flow	kmol/hr									
WATER		0.617	1.689	1.754	1.772	1.778	1.776	1.384	0.297	1.087
SULFU-01		1.164	0.092	0.027	0.009	0.003	0.005	0.397	trace	0.397
SULFU-02		0.443	1.258	1.079	0.844	0.591	0.688	0.297	0.187	0.109
OXYGE-01			0.128	0.250	0.377	0.506	0.457	0.457	0.453	0.004
SULFU-03			0.257	0.500	0.753	1.012	0.913	0.913	0.737	0.176
Mole Frac										
WATER		0.278	0.493	0.486	0.472	0.457	0.463	0.402	0.177	0.613
SULFU-01		0.523	0.027	0.007	0.003	808 PPM	0.001	0.115	4 PPM	0.224
SULFU-02		0.199	0.367	0.299	0.225	0.152	0.179	0.086	0.112	0.062
OXYGE-01			0.037	0.069	0.100	0.130	0.119	0.133	0.271	0.002
SULFU-03			0.075	0.139	0.201	0.260	0.238	0.265	0.440	0.099

Table 4: Input and output concentrations of output stream



3.4 OPTIMIZATION:

After completing simulations successfully it is necessary to optimize the whole process. So initially similar to that of convergence, Section wise optimization is conducted later the final inputs and outputs of the optimized streams will be mentioned. In order to do optimization, initially the basic step is to find the parameter to be optimized and we need to check with respect to this parameter how the efficiency is getting affected. In this Section II part the main parameter which controls the whole simulation is the temperature part and here we took temperature as the parameter for doing optimization and the optimum temperature found to be was 925°C where the decomposition of the Sulfuric acid is maximum. Beyond this temperature, it starts decreasing and hence the

optimum temperature was 925°C. Figure 8 shows a graph showing the optimum temperature against the decomposition of sulfuric acid.

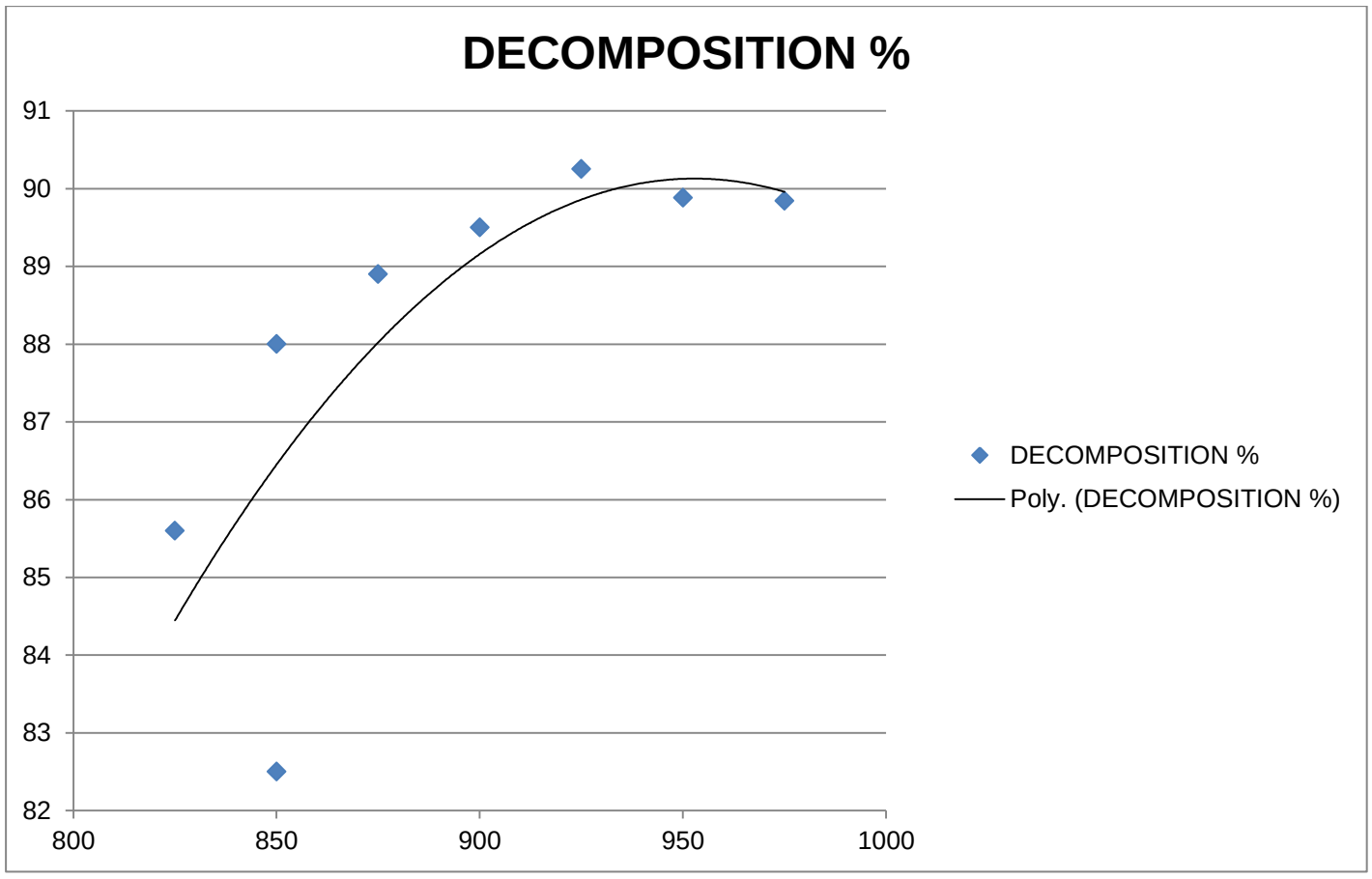


Figure 8: Graph showing optimum temperature of Section II

In the graph X- axis represents the temperature in °C and Y- axis represents the decomposition percentage.

Also one more key parameter need to be optimized in Section II is the amount of energy consumed in section II. Since the reaction occurs at a temperature of 800-950°C, it needs a lot of energy for the reaction to occur effectively. It was found that the hot streams coming out from the decomposition part can be used to concentrate the sulfuric acid coming from the Section I. It was found that the total reaction enthalpy of the sulfuric acid decomposition is 278.643kJ/mol. Hence if such a huge amount of energy is used for the concentration part and thus it is good to reduce the capital cost.

Chapter – 04

Bunsen Reaction of S-I cycle

4.1 SECTION I SIMULATION:

Section I is also known as Bunsen section because in Section I, Bunsen reaction is the major step in the entire process. Bunsen reaction is shown in reaction (4.1)

$$2H_2O+SO_2+I_2 \rightarrow H_2SO_4 + 2HI$$

In section I the main part is the reaction and then separation of the components formed because of the reaction. Jacketed CSTR is used for the Bunsen reaction and then a three phase separator is used to separate the three components that comes from the CSTR. In section I along with H_2SO_4 and HI, other component will also be produced. O_2 which is coming from the Section II is vented off in Section I and then it is recycled back to Section II. H_2SO_4 is a light phase and HI is the dense phase and the Bunsen reaction occurs at a temperature of 100-120°C. This reaction occurs spontaneously and it is an exothermic reaction. Also in this section both the liquid phases are separated and then pumped to Sections II and Section III respectively. Here ELECNRTL is used as a base model for the simulation section. **Figure 9** shows the flow sheet of the Section I. Table 3.4 shows the stream table of the Section I. in this Section I, since it is a bit smaller and the complexity of this plant is not that much high than that of the Section II , the stream table results are validated against the values of GA's flow sheet values. And these values are clearly shown in Table 5. The concentration of the stream resulting after the Bunsen reaction is shown in Table 6. It is clear that the top stream consists of only oxygen and water after which O_2 will be separated from water by increasing the temperatures.

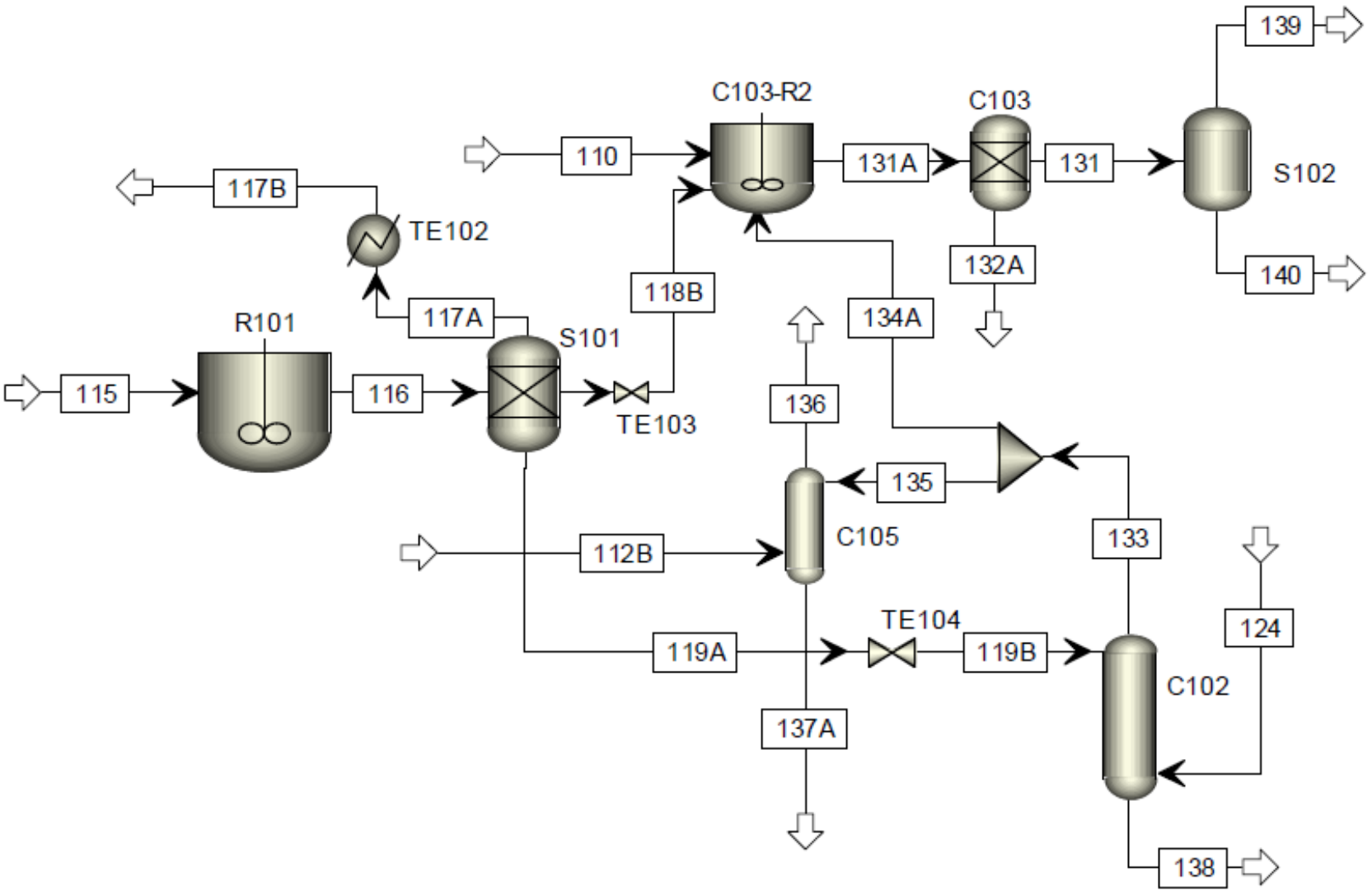


Figure 9: Flow sheet of Section I

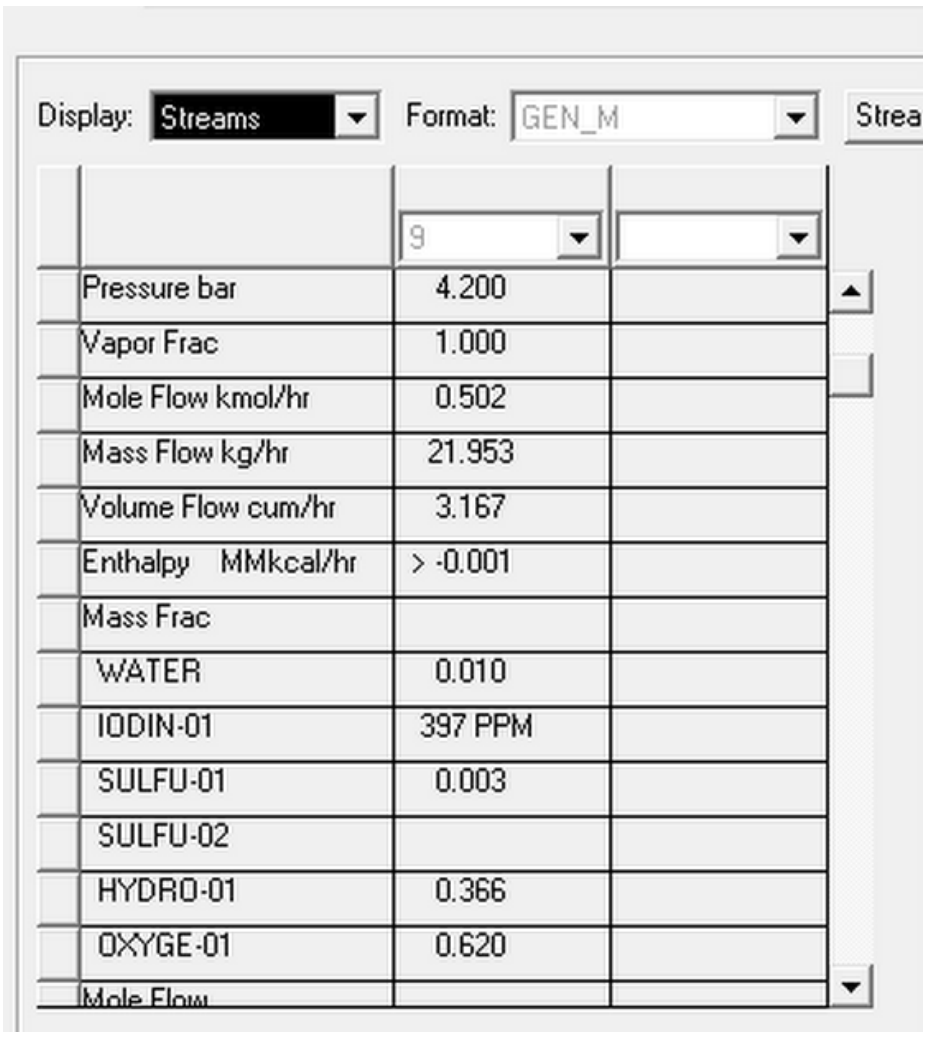
4.2 OPERATING CONDITIONS:

The operating conditions of the Bunsen reactor are 7 bar pressure and 393 K temperature. In section I, along with Jacketed CSTR, other components presented are oxygen scrubber, H_2SO_4 scrubber and HI scrubber to remove the unwanted material.

Table 5: Stream table for Section I

N	Stream	H2SO4 (kmol/h)	HI (kmol/h)	I2 (kmol/h)	H2O (kmol/h)	SO2 (kmol/h)	O2 (kmol/h)	Total (kmol/h)	Phase	Pres.(bar)	Temp. K
1	131	1.015	0	0.019	4.138	0.048	0.016	5.235	L	1.85	384.5
1	GA_131	1.0234	0	0.0184	4.1377	0.0475	0.0155	5.2425	L	1.85	384.5
2	132A	0	0.122	0.811	0.91	0.024	0	1.867	L	1.85	384.5
2	GA_132A	0	0.1389	0.796	0.9252	0.0155	0	1.8756	L	1.85	384.5
3	133	0	0	0.113	0	1.371	0.182	1.667	V	1.85	390.6
3	GA_133	0	0	0.0271	0.3731	1.371	0.1825	1.9537	V	1.85	393
4	135	0	0	0.104	0	1.254	0.167	1.525	V	1.85	390.6
4	GA_135	0	0	0.0248	0.3414	1.2545	0.167	1.7877	V	1.85	393
5	136	0	0	0.006	0	1.254	0.167	1.428	V	1.85	368.2
5	GA_136	0	0	0.0003	0.036	0.0001	0.167	0.2034	V	1.85	369.6
6	137A	0.215	9.982	5.616	67.262	0	0	83.075	L	1.85	369.2
6	GA_137A	0.2173	9.9875	5.5408	67.5643	1.2544	0	84.5643	L	1.85	369.6
7	138	0	12.459	47.921	66.07	0	0	126.451	L	1.85	390.5
7	GA_138	0	12.459	48.0073	65.6973	0	0	126.1636	L	1.85	393
8	139	0.003	0	0.011	0.012	0.048	0.016	0.09	L+V	1.85	384.5
8	GA_139	0	0	0.0184	0.0434	0.0436	0.0155	0.1209	V	1.85	384.5
9	140	1.012	0	0.008	4.125	0	0	5.145	V	1.85	384.5
9	GA_140	1.0234	0	0	4.0943	0.0039	0	5.1216	L	1.85	384.5

Table 6: Top stream of the output



4.3 OPTIMIZATION:

As said earlier, every section needs to be optimized and for this we need to have parameters to do optimization. In Section I, we took pressure and temperatures are selected as parameters which were analyzed whether they are having or showing effect on the overall efficiency of the Section I. it was found after analysis that the change in pressure does not have considerable effect on the overall efficiency. The optimum temperature is found out to be 440K. Figure 10 shows the graph of temperature plotted against the formation of Sulfur dioxide.

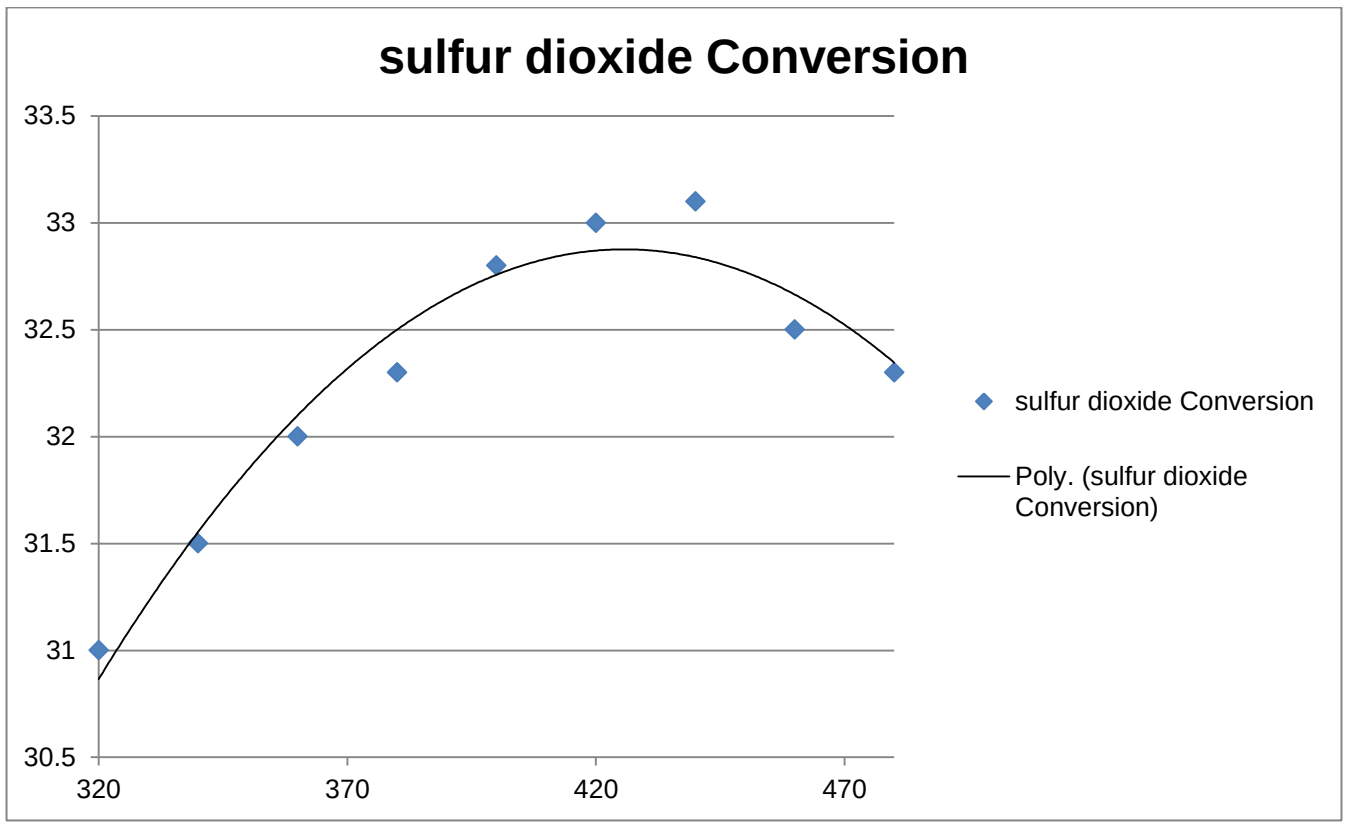


Figure 1: Graph showing optimum temperature value of the Bunsen reaction

In the above graph, X- axis represents the temperature in Kelvin and Y-axis represents the percentage of SO_2 converted. Thus optimization of Section is also completed and the stream table values are successfully validated against the GA's flow sheet.

Chapter – 05

HI Decomposition of S-I cycle

5.1 SECTION III SIMULATION:

Section III is also known as HI decomposition Section. In the entire S-I cycle this particular section plays a very major role in the final production of Hydrogen, because in this section very complex mixtures will form which results in the formation of azeotropes and hence this section needs to be study in detail. The products from the Section I contains two liquid phases and one gaseous phase. The gaseous phase contains most amount of oxygen and it is vented off in Section I and used for other industrial applications. Among the two liquid phases the separation of these phases were done based on the density difference. H_2SO_4 is light in nature and it comes to the top of the separator after prolonged settling. Later HI comes out of the separator and HI is in liquid phase at a temperature of 120°C and at a pressure of around 20 atm. But the product of Section I is not only HI, it contains a mixture of $HI/I_2/H_2O$ and this ternary mixture separation took years for the scientists to develop a proper thermodynamic model to understand the thermodynamics. Later it was found that reactive distillation column can withstand those changes and reactive distillation column has a good ability of undergoing the reaction and distillation simultaneously.

5.2 OPERATING CONDITIONS:

Total No of stages to be considered are 7 in the reactive distillation column. Very High reflux ratio of 20 is considered. It was assumed that the Boil up rate is 210 kmol/hr.

Since the reactive distillation column operates at a temperature of 500-600°C, the bottom product and the side stream product will have very high temperatures and these streams are used to withdraw the energy and it is utilized in different streams to reduce the total energy requirement. The output

product consists of H_2 along with some amounts of water and it is sent to separator to reduce the amount of water present in the top output stream. Figure 11 shows the flow sheet of the Section III.

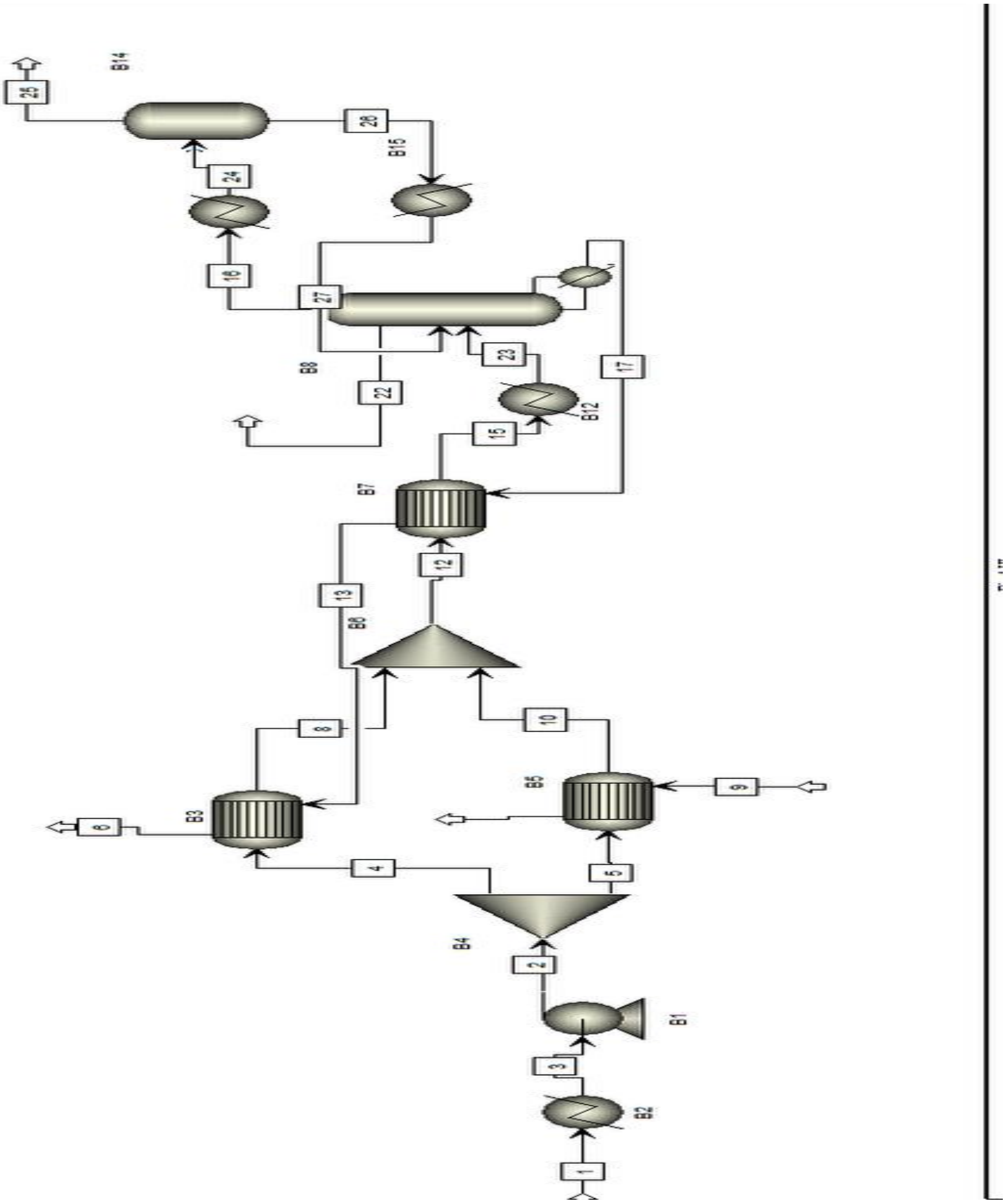


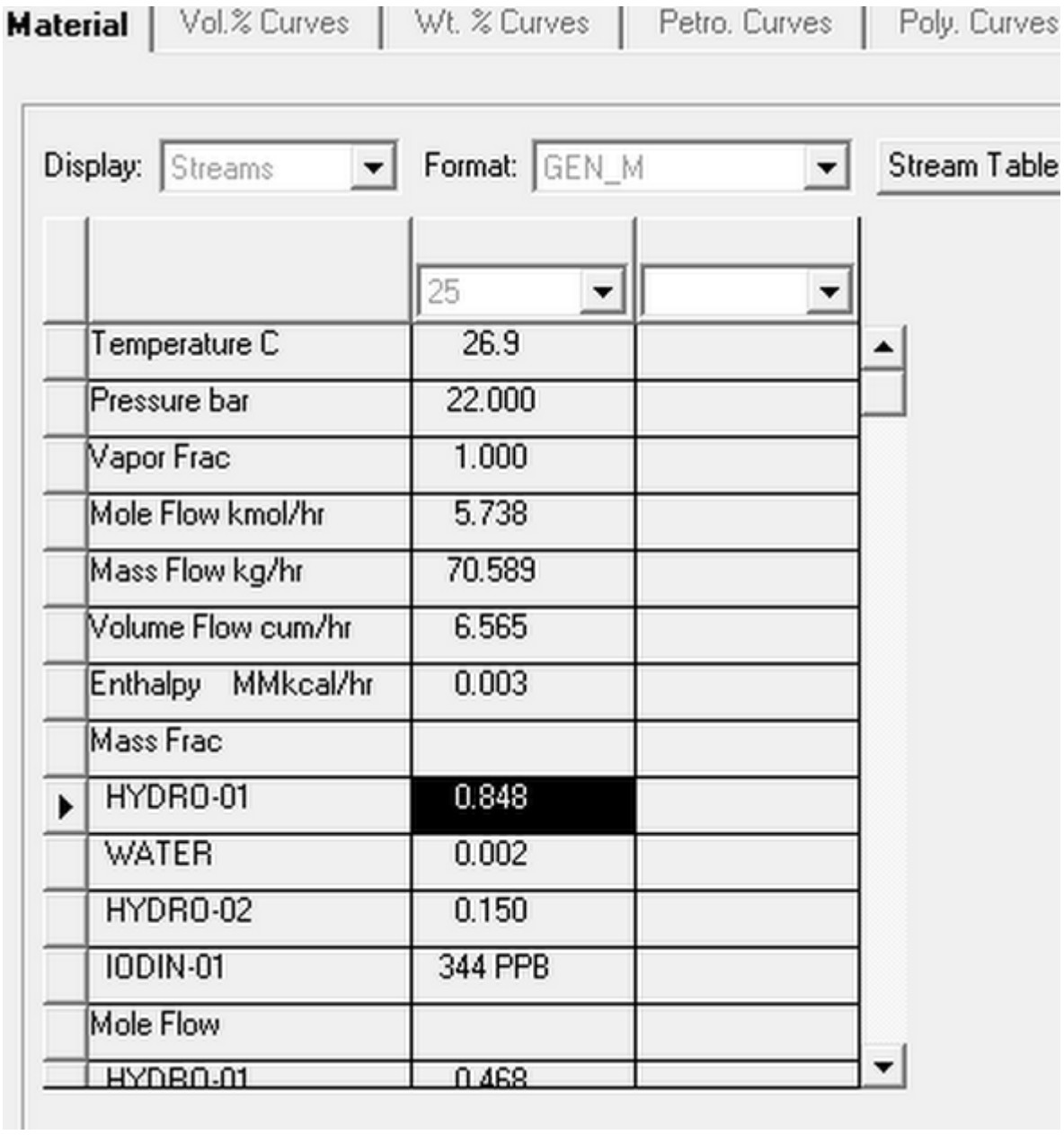
Figure 2: Section III flow sheet

Table 7: Stream table of Section II

Final H																											
Stream ID		1	2	3	4	5	6	8	9	10	11	12	13	15	16	17	22	23	24	25	26	27
Temperature	C	119.8	122.7	120.0	122.7	122.7	130.0	176.9	253.7	150.5	226.8	168.6	248.3	201.1	178.2	324.7	225.2	247.6	19.9	26.9	26.9	220.5
Pressure	bar	1.850	22.000	1.850	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000
Vapor Frac		0.197	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000	0.338	0.448	1.000	0.000	1.000
Molar Flow	kmol/hr	126.163	126.163	126.163	87.492	38.671	43.795	87.492	48.529	38.671	48.529	43.795	126.163	136.163	12.655	43.795	76.630	126.163	12.655	5.738	6.917	6.917
Mass Flow	kg/hr	1496.816	1496.816	1496.816	1037.793	458.024	1001.4.874	1037.793	1090.7.794	458.024	1090.7.794	1496.1.816	1001.4.874	1496.1.816	361.434	1001.4.874	487.6.354	1496.1.816	361.454	70.589	290.845	290.845
Volume Flow	cum/hr	438.968	4.979	4.969	3.453	1.526	2.618	3.654	3.182	1.563	3.105	5.185	2.873	5.358	20.999	3.108	2.385	81.572	6.518	6.565	0.175	11.972
Enthalpy	MMkcal/hr	-3.905	-4.061	-4.068	-2.816	-1.245	-0.099	-2.715	<0.001	-1.218	-0.026	-3.933	0.002	-3.859	-0.287	0.076	-3.831	-3.471	-0.364	0.003	-0.365	-0.293
Mass Frac																						
HTDRO-01		0.107	0.107	0.107	0.107	0.107	0.001	0.107	0.017	0.107	0.017	0.107	0.001	0.107	0.700	0.001	0.036	0.107	0.700	0.848	0.664	0.664
WATER		0.079	0.079	0.079	0.079	0.079	0.008	0.079	0.009	0.079	0.009	0.079	0.008	0.079	0.270	0.008	0.226	0.079	0.270	0.002	0.335	0.335
HYDRO-02							trace						trace		0.029	trace	trace	0.229	0.150	3 PPB	3 PPB	3 PPB
IODIN-01		0.814	0.814	0.814	0.814	0.814	0.990	0.814	0.975	0.814	0.975	0.814	0.990	0.814	746 PPM	0.990	0.738	0.814	746 PPM	344 PPB	927 PPM	927 PPM
Mole Flow	kmol/hr																					
HTDRO-01		12.459	12.459	12.459	8.640	3.819	1.410	8.640	1.410	3.819	1.410	12.459	0.096	12.459	1.978	0.096	1.371	12.459	1.978	0.468	1.510	1.510
WATER		65.697	65.697	65.697	45.560	20.137	5.224	45.560	5.224	20.137	5.224	65.697	4.617	65.697	5.414	4.617	61.072	65.697	5.414	0.008	5.406	5.406
HYDRO-02							trace						trace		5.262	trace	trace		5.262	5.262	trace	trace
IODIN-01		48.007	48.007	48.007	33.292	14.715	39.082	41.895	33.292	14.715	41.895	48.007	39.082	48.007	0.001	39.082	14.187	48.007	0.001	trace	0.001	0.001
Mole Frac																						
HTDRO-01		0.099	0.099	0.099	0.099	0.099	0.002	0.099	0.029	0.099	0.029	0.099	0.002	0.099	0.156	0.002	0.018	0.099	0.156	0.082	0.218	0.218
WATER		0.521	0.521	0.521	0.521	0.521	0.105	0.521	0.108	0.521	0.108	0.521	0.105	0.521	0.428	0.105	0.797	0.521	0.428	0.001	0.782	0.782
HYDRO-02							trace						trace		0.416	trace	4 PPB		0.416	0.917	57 PPB	57 PPB
IODIN-01		0.814	0.814	0.814	0.814	0.814	0.990	0.814	0.975	0.814	0.975	0.814	0.990	0.814	746 PPM	0.990	0.738	0.814	746 PPM	344 PPB	927 PPM	927 PPM

In the above table the concentrations of all the streams present in the Section III are given and the main output stream concentration is shown in Table 8.

Table 8: The final output stream having H_2



From the above figure, it is clear that hydrogen formed is coming from the reaction distillation column and in the output stream is almost pure with around 0.85 mass fraction of pure H_2.

5.3 OPTIMIZATION:

This section also needs to be optimized. In this section it was found that the final output product mainly depends on the operating conditions of the reactive distillation column only. Hence the optimization of Section III is nothing but the optimization of the products of the reactive distillation column. The main

key parameters which affect the reactive distillation are Reflux Ratio, Boil up rate and Side Stream Flow rate.

So all the three parameters were optimized and the concentration of H_2 in final output product is found out by using the optimum values in the simulation.

It was found that optimum value of reflux ratio was 20. At this reflux ratio the amount of H_2 produced is maximum and if it exceeds this value then the lower stages are becoming dry which results in the decrease in the production of H_2. Also same is the case for boil up ratio was found to be 210 kmol/hr. Side stream flow rate was found to be optimum at 76.5 kmol/hr. Using all the three optimum values, the final concentration of Hydrogen was found to be 0.85 mass fraction in the output stream. We can also take number of stages for doing optimization, but an increase in number of plates resulted in the overall capital cost of the plant. Many numbers of simulations were conducted to found the optimum set for the production of Hydrogen.

Chapter – 06

Conclusion and Future Work

6.1 CONCLUSION AND RECOMMENDATION:

The whole Sulfur Iodine thermochemical cycle has been simulated using ASPENPLUS simulation program with ELECNRTL as a base thermodynamic model in all the three sections. All the three sections were successfully simulated and they are validated against the GA's flow sheet values. It was found that the final amount of hydrogen produced is 4 kmol/hr for an input of 10 kmol/hr which means that the efficiency is around 40%. Hence we need to improve this model further for better efficiency. The overall efficiency of the GA's flow sheet was found to 51%. Main advantages of using these thermochemical cycles are all the products will get recycled back to the cycle and water is the only component that is consumed in the entire cycle.

Efficiency can be further increased by taking more number of parameters for optimization. In Section I, temperature and pressure were only considered as optimization parameters. But there are other parameters which will also show some effect in the production of sulfuric acid and hydrogen iodide. We can consider the reaction rate and its dynamics to increase more efficiency. Similarly for other two sections also, we need to keep focus on the reaction dynamics.

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